SUBJECT INDEX

ACCORDION
  for AK reaction pathway 141
  in CK reaction rate 145
  in rate-constant determinations 133
O-(2-Acetamido-2-deoxy-α-D-galactopyranosyl)-L-serine (α-GalNAc→Ser)
  anomeric configuration 312, 313, 318, 323
  ^{13}C NMR spectrum 311
  chemical shift data 312
O-(2-Acetamido-2-deoxy-α-D-galactopyranosyl)-L-threonine (α-GalNAc→Thr)
  anomeric configuration 313, 318, 323
  ^{13}C NMR spectrum 311, 313
  chemical shift data 312
Acetonitrile
  ^{13}C and ^{15}N chemical shifts 331
  ^{14}N–^{1}H coupling 287–289
  -water solvent system 376, 378
Acetylchloride Cl–C couplings in 294
α-*N*-Acetylneuraminic acid (α-NeuAc) 309
N-Acetyl-L-phenylalanyl-glycinal inhibition of papain 40, 41
N-Acetyl-L-tryptophan binding to chymotrypsin 30
N-Acetyl-L-tyrosine semicarbazide and ligand-substrate equilibrium 31
Acyl intermediates, observation under cryoenzymological conditions 45–51
Acylation of enzymes 34
Adenylate kinase (AK, nucleoside-5′-triphosphate: nucleoside-5′-monophosphate phosphotransferase, EC 2.7.4.3)
  active site studies 141
  ^{19}F NMR 144
  ^{1}H NMR 140–143
  His-36 significance 141–144
  ^{31}P NMR 139
  reaction catalysed 139
  substrate binding 166
ADP (adenosine diphosphate)
  sulphur substituted 136
    Mg and Cd complexes 137
    myosin S1, ^{18}O exchange and 154
^{27}Al
  –^{81}Br coupling constant 296
  –^{35}Cl coupling constant 291
  –^{14}N coupling constant 288
  NMR
    complexes 338, 339, 372
    hydrolysis of Al^{3+} 337, 338
    in mixed solvents 379
    –Ni^{2+} interaction 356, 357
Al^{3+} solvent exchange by ^{1}H resonance 385
Alcohol dehydrogenases ^{13}C NMR 15, 16
Alkali metals
  chemical shift studies
    anions 336
    cations 334, 335
  ^{1}H exchange in aqueous solutions 388
  halides and water association parameters 350, 351
  quadrupole relaxation rates
    concentration effects 369
    data 366, 367
    in mixed solvent systems 374–378
    isotope effects 374
Alkaline earth metals
  chemical shift studies 337
  quadrupole relaxation rates 366, 368
    concentration effects 371, 372
    isotope effects 374
Alkaline phosphatase (AP, orthophosphoric monoester phosphohydrolase, EC 3.13.1)
  ^{13}C enriched 11
  metal complexes 156, 157
  reaction catalysed 155, 156
  transferase activity 157
p-Amidinophenylpyruvic acid (APPA)
  inhibition of trypsin 37
    scheme 39
  structure 38
Amino acids, ^{13}C enriched, incorporation into enzymes 9
Aminopterin binding to DHFR 21, 22, 24, 25
Antigen T_N *see* T_N antigen
Arginine kinase (AK, phosphoarginine: ADP phosphotransferase, EC 2.7.3.3) 147
^{75}As coupling constants 300
Aspartate transcarbamylase ^{13}C NMR 10, 13
  and PALA inhibition 13
ATP
  cleavage by ATPase 158
  ^{17}O NMR of Mg^{2+} complexes 138
  ^{18}O and CK 145
  ^{31}P NMR of sulphur substituted 138
  –PK complexes 146, 147
ATPase 158

^{11}B coupling constants, table of 284, 285
Bacterial luciferase, cryoenzymological ^{13}C NMR 51–53
3-Benzyl-6-chloro-2-pyrone as chymotrypsin suicide substrate 29, 31
N-α-Benzyloxycarbonyl-L-lysine-*p*-nitrophenyl ester (Z-lys-pNP) trypsin catalysed hydrolysis of 46
^{209}Bi quadrupole relaxation 381
BLEW-6 cycle 113
BLEW-12 cycle 112
^{81}Br
  –^{13}C coupling non-exponential relaxation

decay 282
coupling constants 293, 295–298
quadrupole relaxation 379
Bromoacetates, ^{13}C, alkylation of carbonic anhydrase 26
Bromobenzene ^{13}C relaxation in 298

^{13}C
coupling
B 285, 286
Br 282, 296
Cl 290, 291, 294
I 299
N 287, 288, 290
crotonaldehyde spectra 103, 104
-enriched nuclei, signal resolution 6
enrichment of enzymes
biosynthetic incorporation of amino acids 9, 28
carboxymethylation 12
chemical synthesis 7
enzymatic synthesis 8
guanidation reactions 12
methionine residues 8
reductive methylation 11
thiol group cyanalation 12
^{13}C NMR
^{18}O shift study 391
of cations in DMF complexes 331
of enzymes *see also* individual enzymes
alcohol dehydrogenases 15
AP 157
aspartate transcarbamylase 10, 13
carbonic anhydrase 25–27
carboxypeptidase A 20
citrate synthetase 14
dihydrofolate reductase 9, 11, 21–25
fructose-1,6-diphosphate aldolase 15–17
β-galactosidase 11
glutamine synthetase 18
GP 162
β-hydroxydecanol-thioester dehydrase 18
myosin 153
natural abundance 7
papain 39–42, 49–51
serine dehydratase 17
serine proteases 27–39, 45–49
under cryoenzymological conditions 45–51
of glycophorins
chemical shift data for α- and β-glycosyl amino acids 312
α-GalNAc→Ser 310, 311
α-GalNAc→Thr 311, 313
β-Gal-(1→3)-α-GalNAc→Ser 313–315
β-Gal-(1→3)-α-GalNAc→Thr 314, 315
glyco-octapeptides A^M and A^N 322
glycoprotein structure and 310, 311
model glycopeptides 316–320
N-terminus and 309
T antigen 321
T_N 321, 322
signal/noise 6
^2H substitution and 7
solvent chemical shifts 329
^{13}C relaxation in macromolecules 2
chemical shift anisotropy (CSA) 4
linewidths (W) 3, 6
rotational correlation times 3–5
spin-lattice relaxation time (T_1) 3
transverse relaxation time (T_2^*) 6
$CaCl_2$ water association parameter 351
Carbonic anhydrase ^{13}C NMR
carboxymethylation 26
cobalt substitution and 27
inhibition by HCN 25
reaction catalysed 25
Carboxypeptidase A ^{13}C NMR 20
Carr–Purcell spin-echo sequence
B–H coupling and 284
Cl–C coupling and 294
for chemical exchange studies 383
N–H coupling and 288
O–H coupling and 301
T_2 measurement 281, 289
^{113}Cd
NMR of AP 156
–^{17}O coupling 300, 301
Chemical shifts and J coupling
anisotropy and relaxation 382
quadrupolar relaxation and 346
selective solvation, table of 345
solute nuclei 332
alkaline earth metals 337
alkali metal anions 336
alkali metal nuclides 334, 335
^{13}C 333
group III nuclides 337
groups IV, V and VI nuclides 339
^1H 333
halogens 336
N 333
^{17}O 333
transition metal nuclides 340
solvent shifts 329
acetonitrile 331
DMF 331
liquid ammonia 332
methanol 331
requirements for structural information 330
Chemically induced dynamic nuclear polarization (CIDNP), light induced, principles and application 128, 138, 148
Chlorobenzene ^{13}C–^{35}Cl couplings in 294
Chloromethylketone inhibitor Z-lys-CMK
inhibition of trypsin 34–38
structure 35
2-Chloro-2-methylpropane C–Cl couplings in 294
Chymotrypsin ^{13}C NMR *see also* Serine proteases
active site chemical modification 28
acyl intermediates 31–33, 49
chloromethylketone inhibition 34
ligand–substrate binding equilibrium 30
p-nitrophenyl acetate and 32, 33

reaction catalysed 28
suicide inhibitors 29–31
Citrate synthetase ^{13}C NMR 14
C_l coupling constants 290–295
^{35}Cl
chemical shift and quadrupole relaxation rate 346
exchange rate in aqueous chloride 389, 390
field gradient fluctuations in quadrupole relaxation 362, 363
Ni^{2+} coordination 359
quadrupole relaxation in polyatomic ion 379
^{59}Co
chemical shift studies 341, 342
–^{14}N coupling 288
quadrupole relaxation in polyatomic ions 380, 382
Co^{2+} solvent exchange at 386
Composite pulses
1- 3–3–1 sequences 62
2–1–4 Redfield sequences 62
90° comparisons 89, 91
$90_{90}180_{0}90_{90}$ non-ideal 63, 64
180°
B classes coalescence 88, 90
comparisons 90, 94
in anisotropic systems 112, 113
numerical evaluation 97
r.f. compensated 97, 98
resonance offset compensated 98
bilinear rotations 109
coherence order selection 108
coherences manipulation 102
INADEQUATE and 103, 104
WALTZ and 103
DANTE sequence 62
double-quantum spectroscopy 100
ESR and 110
Hamiltonians manipulation 102
in anisotropic media
BLEW-6 113
BLEW-12 112
coherent averaging 111
consecutive rotation 114
broadband population inversions 116
design of 90° sequence 115
quadrupole echo sequences 116, 117
double quantum excitation 118
phenylalanine ^{2}H lineshapes 113, 117
quadrupolar order 119
symmetrizing 112, 113
windowless cycles 112
optical spectroscopy and 86, 110
population manipulation 101
practical implementation 105
r.f.
field selection 106
pulse considerations 62
self-compensation 63
solvent suppression 62
theory
continuous modulation 84
far off-resonance behaviour 85
in coherent laser spectroscopy 86
geometrical
9-element composite 180° 72, 73
$90_{90}90_{0}$ 71, 73
$90_{180}180_{120}$ 72
$90_{180}180_{300}$ 71
second-order compensation 72
spin-knotting 72, 73
non-commuting rotations 76–78
propagator compensation 73
Magnus expansion 74, 75
sequence compensation 76
recursive expansions
broadband cycles 78, 81, 112
inverse formation 80
MLEV-16 80
of 90° pulses 80–82
of 180° pulses 81–83
WALTZ-16 79, 80, 102
Waugh expansion 78, 79
symmetry properties 84
transmutations 83
type A 86, 87
90° 89, 91, 92
180° 90
supplementary z-rotation 99
usage 99, 101, 111
type B_1 86, 87
90° 89, 91, 93
supplementary z-rotation 99, 100
usage 99, 101, 111
type B_2 87
90° 89, 91, 94
usage 99, 101, 111
type B_3 87
90° 89, 91, 95, 96
usage 99, 101, 111
virtual 110
z-pulses 107
COSY
^{1}H spectrum of AK 141, 142
sequence 126
^{53}Cr quadrupole relaxation 379
Creatine kinase (CK, adenosine-5′-triphosphate: creatine phosphotransferase, EC 2.7.3.2)
^{1}H NMR 146
^{31}P NMR 144
metal complexes on 145
reaction catalysed 144
Cross-relaxation spectroscopy 248–255
Cryoenzymological ^{13}C NMR
cryosolvent choice 42, 44
intermediates
criteria for observation 42, 45
from bacterial luciferase 51
from papain 49
from phenylalanine hydroxylase 52
from trypsin 46–48
optimizing accumulation of 43, 44
possible errors of interpretation 55
thermodynamics 44

^{63}Cu complexes
chemical shifts 342, 343
linewidths 380, 381

DANTE sequence 62
Dihydrofolate reductase (DHFR) ^{13}C enriched NMR 9, 11, 21
conformational equilibria 22
folate interaction and 24
inhibitor binding and 21, 22, 24
$NADP^+$ binding to 22–24
N,N-Dimethylformamide (DMF)
cation interactions 331
exchange on $[Ln(DMF)_8]^{3+}$ 387
–water solvent system 379
Dimethylsulphoxide (DMSO)
as cryoenzymological solvent 44, 46, 49
–water solvent system 379
Dipole–dipole relaxation *see* nuclear magnetic relaxation of simple electrolyte solutions
Double quantum (DQ) spectroscopy 127
advantages over COSY 128
^{1}H of AK 141, 142

Electrochemistry, application of NMR 393–397
Electrolyte solutions
cation binding of solvent nuclei 329
concentrated (hydrous melts) water ^{1}H relaxation 351
NMR during current flow 393
detection of moving boundaries 396
ion transport 394
spin-echo sequence for 395
Elongation factor Tu (EF-Tu)
^{1}H NMR 159
^{31}P NMR 159, 164
properties 159
Enzymes *see* ^{13}C NMR of, Phosphoryl-transferring, individual enzymes
E.S.R. composite pulses in 110
Ethanol in lithium halide solutions, molecular groups B′ coefficients 348
Exchange processes in electrolyte solutions
experimental
anion exchange parameters 389, 390
^{1}H exchange in aqueous solutions 387
salt concentration on 388, 389
^{18}O isotope shift 390, 391
pressure and temperature effects 391–393
solvent ^{1}H resonance 385–387
water exchange 392
theory
Bloch equations 383, 384
Carr–Purcell sequence 383
electric circuit analogy 387
$T_{1\rho}$ temperature dependence 384

^{19}F NMR
–^{79}Br coupling 296
–Cl coupling 291
–^{14}N coupling 288, 289
of AP 157
of 2′-fluoroadenosine 138
of GP 163
of myosin 152, 153
$^{19}F^-$
relaxation rate measurement 353
water orientation and 352
Field-cycling NMR (FC)
advantages 173, 176
alternative techniques and limitations
rotating frame 212
tunable spectrometers 211
areas of application 229
basic requirements 174
conflicting requirements, solid and liquid samples 201
cycle requirements 194
dipolar (spin) decoupling 259
fast field rotation 260
nematics 260
earth's field technique 225
electronic field switches 180, 201
capacitor requirements 193
characteristics 181
cryomagnet limit 184, 188
diode combinations 192, 193
energy consumption and dissipation 189–194
energy storage 185, 186, 190
modified turn-off characteristics with protection 193
parameters 191
power requirements 190
RLC network 187–189
simple design, current-time course 182, 183, 190
varistor characteristic 184, 185, 191–193
voltage transient suppression 191–193
fast adiabatic cycle
ideal 194
adiabatic (slow) limit 195
build up and decay of magnetization 195, 196
generalized 196
inverse spin temperature development 196, 198
non-relaxation (fast) limit 195
real 199
turn-on interval 200
field compensation 226
field rotation 228
frequency range 176
level crossing and cross-relaxation spectroscopy 248
quadrupole spectrum and 252
quantum tunnelling 254, 255
theory 249
value of technique 250
magnets
air-core coil configurations 216, 217
mathematics 216

practical details 218
speed characteris... 213
table of data 214, 215
mechanical field switches 178, 179
multi-step cycles 227
possible experimental programmes 202
cross-relaxation (T_c) 207–209
diffusion (D) 206, 207
longitudinal relaxation (T_1) 202–204
pure quadrupole resonance (ν_Q) 209–211
transverse relaxation (T_2) 204–206
power supplies, switches and damping elements
circuits with energy storage 221
GTO switches 221–223
MOSFETs 224, 225
circuits without energy storage 219, 220
principles 175
relaxation spectroscopy 202–209, 229
experimental 242
biological systems 244
^{1}H exchange in water 261–263
ionic and molecular crystals 248
liquid crystals and nematics 245, 246, 254, 260, 263–267
low molar mass liquids 243
metals 247
oligomers and polymers 246
organic conductors 247
paraffin $C_{19}H_{40}$ 267–270
paramagnetic solutions 244
parameters from model fits 269
reorientations in nematics 263–267
theory 230
asymptotic behaviour (T_1) table 240, 241
dispersion table 236, 237
models 230
power spectra table 238, 239
single spin temperature 232, 233
T_1 231–233, 235–237, 240–245
T_2 231, 232, 234, 236, 237
sensitivity gain 177, 178
zero-field
dipole resonance spectra 258
Fourier transform 256
pure quadrupole resonances 255, 258
superconductors 255
theoretical aspects 256, 257
Flavin mononucleotide (4α-^{13}C) reduction and luciferase interaction 51, 52
2-Fluoropyridine ^{14}N–^{19}F coupling 288, 289
Folate binding to DHFR, protonation states and 24
Fructose-1,6-diphosphate aldolase ^{13}C NMR 15
reaction sequence and 16, 17

^{69,71}Ga
chemical shifts 338, 339
–^{35}Cl coupling 291
–^{14}N coupling 288

β-Galactosidase ^{13}C (enriched) NMR 11
GDP (guanosine diphosphate ^{31}P NMR of sulphur-substituted complexes 136, 137
Glucokinase (GK, ATP: glucose-6-phosphotransferase, EC 2.7.1.2) ^{31}P NMR 148
Glutamine synthetase ^{13}C NMR 18
Glycogen phosphorylase (GP, α-1,4-glucan: orthophosphate glucosyl transferase (EC 2.4.1.1)
AMP activation 160
^{13}C NMR 162
^{19}F NMR 163
from various sources 162
^{1}H NMR 162
^{31}P NMR 160–162
reaction catalysed 159
role of pyridoxal-5′-phosphate 160–163
structural forms 159, 160
Glyco-octapeptides A^M and A^N
chemical shift data 322
structures 324
Glycopeptide β-Gal-(1→3)-α-GalNAc→Ser
anomeric configuration 315
^{13}C NMR spectrum 314
chemical shift data 315
glycophorin A attachment 309
structure 314
Glycopeptide β-Gal-(1→3)-α-GalNAc→Thr
anomeric configuration 316
^{13}C NMR spectrum 314
chemical shift data 315
glycophorin A attachment 309
structure 315
Glycopeptides (*see also* Pentapeptide) ^{13}C NMR studies 316–320
Glycophorin $A^{(M\text{ and }N)}$
A^M
-related pentapeptide ^{13}C NMR studies 316–320
relation to T_N 320
amino acid sequence 308
^{13}C NMR 309
carbohydrate structure 308
distinction between A^M and A^N 308
properties 307
tetrasaccharide attached to 308, 309
Glycophorins, general description 307
Glycoproteins ^{13}C NMR spectra 310, 311
Glycosylation on protein structure 319
Group III nuclides, chemical shift studies 337
^{27}Al 337–339
Ga 338, 339
Groups IV, V and VI nuclides, chemical shift studies 339
^{209}Bi 340
^{31}P 340
^{33}S 340
^{29}Si 339
GTPase activity of c-Ha-ras oncogene product p21 163

^{1}H
chemical shifts
$-^{2}H$ fractionation factors 332
of cations in DMF 331
of ions in MeOH 331
coupling
$-^{11}B$ 284, 285
$-^{81}Br$ 296
$-^{35}Cl$ 290, 292
$-^{14}N$ 287, 288
$-^{17}O$ 300
dipole transitions, zero field 258
exchange in aqueous solutions 261–263, 387
NMR
of AK 140–143
of c-Ha-ras oncogene product p21 163
of CK 146
of EF-Tu 159
of GP 162
of myosin 154
of nucleoside-5′-phosphates 135
of PGK 148
of PKs 146
of PTS 150
relaxation
exchange processes and 385
in biological systems 244
in F^- solutions 352, 353
in hydrous melts 351
in mesogens 246, 263–267
in organic conductors 247
in paramagnetic and diamagnetic solution 358, 359
in paramagnetic systems 244
in polymers 246, 253
intermolecular 354
quadrupolar dips 253
solvent resonance 385
^{2}H–^{2}H interaction, spin distance and 352–354
$^{2}H_2O$–$^{1}H_2O$
effect on relaxation of alkali halides 373
effect on various ionic nuclei 341, 374
c-Ha-ras oncogene product p21 163
Halides
anion exchange parameters 390
chemical shift studies 336
linewidths 371
quadrupole relaxation
concentration effects 369
data 366
Halogen–phosphorus coupling constants 290–300
Hexamethylphosphoric triamide (HMPT)–water solvent system 376–378
Hexokinase (HK, ATP: hexose-6-phosphotransferase, EC 2.7.1.1) 148
^{109}Hg quadrupole relaxation 382
Hydrogen cyanide inhibition of carbonic anhydrase 25
Hydronium ion, ^{17}O spectrum 343, 344
β-Hydroxydecanol-thioester dehydrase reactions ^{13}C NMR 18, 19
Hydroxyflavin intermediate, cryoenzymological conditions 51, 52
Hydroxypterin intermediate, cryoenzymological conditions 52–55

^{127}I coupling constants data 298–300
INADEQUATE
relation to DQ 127
sequence and advantages 103, 104
Ionic
internal pressures and water ^{1}H chemical shifts 330
mobilities, NMR measurement 395

Laser spectroscopy, off-resonance effects 86
^{7}Li
chemical shifts in various solvents 334, 335
CK relaxation studies 147
Ni^{2+} interaction 356
quadrupolar relaxation
field gradient fluctuations 362, 363
rates 367, 378
zero-field quadrupole resonances 258
Liquid crystals
Field cycling studies 245, 253, 260, 263
field rotation 259
Locking-field strength $T_{1\rho}$ dependence 281, 293–295
Low-frequency NMR advantages 173
Lysozyme ^{13}C NMR 7
cryoenzymological 45

Magic angle spinning (MAS) theory 259
MBBA (p-methoxybenzylidene-p-n-butylaniline)
^{1}H T_1 dispersions 246, 256, 266, 269
reorientations in 264
spin decoupling 260
Mesogens *see* Nematics
Metals field cycling studies 247
Methanol molecules lifetimes and CH_3 relaxation rate 386
Methionine residues ^{13}C enrichment
biosynthetic incorporation 9
direct chemical replacement 8
Methotrexate binding to DHFR 21, 22, 24, 25
Mg^{2+}
nucleoside complexes 135–138
on AK reaction rate 139
Mixed solvents
quadrupolar relaxation in 374–379
selective solvation in 345
MLEV-16 80
MN blood-group determinants
antigen location 309
structure possibilities 324
^{55}Mn
^{18}O isotope effect 390
quadrupole relaxation 379
Mn^{2+}

as relaxation agent 393
solvent exchange at 385
Mo quadrupole relaxation 379
Multipulse spin-flip narrowing 259
Myokinase *see* Adenylate kinase
Myosin
^{13}C NMR 154, 155
^{19}F NMR 152, 153
^{1}H NMR 154, 155
molecule and proteolytic fragments 152
S1 fragment 152–155
^{18}O exchange 154, 155
^{31}P NMR 152, 164

^{14}N
chemical shifts in liquid ammonia 332, 380
coupling constants 287–290
^{15}N
/^{14}N isotope effect 333
NMR of nucleosides 138
^{23}Na
chemical shifts in various solvents 335, 336
hydration 370
NMR of moving boundary 396
quadrupole relaxation
field gradient fluctuations 362, 363
rates
in mixed solvent systems 375–378
Na^+ and Na^- 367
Nematics *see also* MBBA and PAA
^{1}H T_1 dispersion in 246, 253, 254, 264, 265
reorientations in 263–267
spin decoupling 260
Ni^{2+}
Cl^- coordination 359
interaction with other cations 356, 357
p-Nitrophenyl [1-^{13}C] acetate hydrolysis, chymotrypsin catalysis 31–33
Nuclear magnetic relaxation of simple electrolyte solutions (*see also* Quadrupolar relaxation) 346
dipole–dipole 347
of solute nuclei
F^-–methanol interaction 353
F^-–water interaction 352
of solvent nuclei
A-parameter 348–351
B-' coefficients 348
during current flow 396
extreme narrowing condition and 347, 360
paramagnetic
addition of diamagnetic salt 358, 359
Al^{3+}–Ni^{2+} interaction 356, 357
application of PRE 359
frequency dependent 358
ion charge on dynamic properties 357
Li^{2+}–Ni^{2+} interaction 356
rate measurements 357, 358
reduced spectral density curves 358
slow motion problem 355
Solomon–Bloembergen equations and 354–356
quadrupole
experimental 365–382
theory 360–365
NOESY
sequence 127
use in rate constant determinations 132
Nuclear Overhauser effects (NOE)
in AK active site studies 141
in ATPase studies 158
in CK studies 146
Nucleoside-5'-phosphates and metal complexes 135, 136, 138
Nucleoside triphosphatase and ^{16}O, ^{18}O exchange 129

^{17}O
coupling constants 300–302
H_3O^+ 344
solvation studies 331
^{18}O
exchange studies 129, 130, 154, 155, 158, 391–393
lability in phosphoryltransfer studies 133, 134, 145, 147
Oligosaccharide attached to glycophorin A polypeptide 309
Optical spectroscopy, composite pulses in 110
Organic conductors ^{1}H F.C. relaxation studies 247

^{31}P
–Br coupling 296
–Cl coupling 291, 292
–mixed halides coupling 293, 294, 297
NMR
chemical shift values of nucleotide diphosphate complexes 164
in phosphoryltransfer stereochemistry 133
of AgK 147
of AK 139
of AP 156
of ATPases 158
of c-Ha-ras oncogene product p21 163
of CK 144
of EF-Tu 159
of GK 148
of GP 160
of HK 148
of myosin 152
of NTPase reactions 130, 131
of nucleoside-5'-phosphate–metal complexes 135
of PCK 165
of PEPS 165
of PGK 147
of PGM 164
of PK 146
of POD 165
of protein kinases 150

PAA(*p*-azoxyanisole) ^{1}H T_1 relaxation dispersion 246, 253, 254, 264, 265, 269
Papain ^{13}C NMR
  catalytic triad 39
  cryoenzymological conditions
    acyl intermediates 45, 49
    benzoylimidazole hydrolysis 49–51
  cryosolvents 44
  inhibition 40, 41
Paraffin $C_{19}H_{40}$
  molecular motions in solid 267
    models for 268–270
Paramagnetic solutions relaxation spectroscopy 244
^{207}Pb–Cl coupling 291
Pentapeptide Ser-Ser-Thr-Thr-Gly
  triglycosylated *see* T_N antigen
  various monoglycosylated
    ^{13}C chemical shift 317–319
    ^{13}C spin lattice relaxation times 319
    structures 316
    titration data 316, 319
Pepsin ^{13}C NMR 19, 20
Pepstatin inhibition of pepsin 19
d^8-Phenylalanine ^{2}H lineshapes 113, 117
Phenylalanine hydroxylase, cryoenzymological ^{13}C NMR 52–55
Phenylmethanesulphonyl fluoride [methylene-^{13}C] modification of trypsin 28
Phosphoenolpyruvate carboxykinase (PCK, GTP: oxaloacetate carboxylase (transphosphorylating), EC 4.1.1.32)
  ^{31}P NMR 165
  PRE measurements 164, 165
  reaction catalysed 164
Phosphoenolpyruvate-dependent phosphotransferase system (PTS, PEP: sugar phosphotransferase system)
  ^{1}H NMR
    of Factor 3 151
    of HPr 150
  ^{31}P NMR 150, 151
  reaction scheme 150
Phosphoenolpyruvate synthetase (PEPS, EC 2.7.9.2) 165
Phosphoglucomutase (PGM, EC 2.7.5.1) 164
3-Phosphoglycerate kinase (PGK, 1,3-bis-phosphoglycerate: ADP phosphokinase, EC 2.7.2.3)
  ^{1}H NMR 148
  ^{31}P NMR 147
  reaction catalysed 147
N-Phosphonacetyl-L-aspartate (PALA) on aspartate transcarbamylase ^{13}C NMR 13, 14
Phosphoric ester hydrolases 151–164
Phosphoryltransfer
  bond-breaking and making sequences 133, 134
  stereochemistry 133
Phosphoryl transferring enzymes NMR studies 139–166 (*see also* individual enzymes)
  CIDNP 128
  rate constant determinations 128
    isotope exchange studies 129
    lineshape calculations 129
    magnetization transfer 131
    nucleoside triphosphate cleavage 129–131
    spin-echo pulse sequence 131
    two-dimensional 132
  suitable enzymes for 124
  suitable nuclei for 124, 125
  two-dimensional 125, 132
    COSY 126
    NOESY 127
    double quantum (DQ) 127
Polymers ^{1}H field cycling relaxation studies 246
Protein kinases (ATP: protein phosphotransferase, EC 2.7.1.37)
  ^{31}P NMR 150
  PRE studies 149
  reactions catalysed 149
Proton (*see* ^{1}H) relaxation enhancement (PRE)
  paramagnetic ion solutions and 359
  protein kinase studies 149
Pyridozal-5′-phosphate in GP activity 160
  analogues 162
Pyrimethamine binding to DHFR 21, 25
Pyruvate kinases (PK, phosphoenolpyruvate: ADP phosphotransferase, EC 2.7.1.40)
  ^{1}H NMR 146
  ^{7}Li NMR 147
  ^{31}P NMR 146
  reaction catalysed 146
Pyruvate, orthophosphate dikinase (POD, EC 2.7.9.1) 165

Quadrupolar relaxation
  ionic nuclei
    experimental
      activation energies and 369
      applied electric field effect 397
      by chemical shift anisotropy 382
      concentration effects 369–373
      dilute solutions 365
      dynamic solvent isotope effects 373
      monatomic ions in mixed solvents 374–379
      polyatomic ions 379–382
      rates for ions in various solvents 366
      solvation shell symmetry 367
    theory
      comparison with experimental data 364
      continuum model 362
      field gradient fluctuations 362, 363
      fully oriented solvation model 361
      in complexes and polyatomic ions 364, 365
  spin coupling constants and data
    As, Sb and U 300
    B 284, 285
    Br 295–298
    Cl 290–295
    I 298–300

N 286–290
O 300–302
echo sequences 116, 117
relaxation
extreme narrowing condition 278
fast relaxation 279
intermediate relaxation rates 278
non-exponential decay analysis 282, 298
scalar relaxation of the first kind 283
scalar relaxation of the second kind 295
T_1 and T_2 measurement 279, 280, 302
$T_{1\rho}$ and locking field strength 281, 293, 294, 303
T_2 and pulse repetition rate 281, 289
Quantum tunnelling, cross relaxation spectroscopy and 254, 255

Rb
halides
ion configurations 370
water–water association and 350
quadrupolar relaxation 367, 376, 378
^{187}Re quadrupolar relaxation 379
Red blood cell glycophorin A interaction 308
Relaxation spectroscopy *see* Field-cycling NMR *and* Quadrupolar relaxation
Ribonuclease
^{13}C enrichment 7, 8
^{13}C NMR 7
^{1}H NMR in cryosolvents 55
Rotating frame experiments compared with field cycling 212
^{99}Ru
chemical shifts of complexes 342
self-exchange reaction study 393

^{33}S quadrupole relaxation 379, 381, 382
^{121}Sb–^{19}F coupling 300
Self diffusion coefficients, A parameter and 350
Serine dehydratase ^{13}C NMR 17
Serine proteases ^{13}C NMR
active site chemical modification 28
acyl intermediates 31–34, 46
catalytic triad 27, 28
inhibition schemes 35, 37–39
ligand-substrate binding equilibrium 30
minimal three-step process 27, 43, 46
suicide inhibitors of chymotrypsin 29–31
tetrahedral adducts and 34, 35, 38
transition state analogues 34
^{29}Si
chemical shifts 339
–^{35}Cl coupling 291, 295
Single pulse theory
ideal pulses 67
non-ideal pulses 68
off-resonance effects 69, 70
phase and shape errors 69
r.f. inhomogeneity 69
pulse propagators, conventions 66
^{119}Sn
–^{81}B coupling 296, 297
–^{35}Cl coupling 291, 292
–^{127}I coupling 299
Solvation numbers, chemical shift studies and 329, 331, 345
Spin coupling constants *see* Quadrupolar relaxation
Spin-echo, pulsed gradient sequence for ion transport studies 395
Spin–spin coupling in polyatomic ions
constants, table of 344
hydronium ion characterization 343, 344

T antigen
exposure, glycophorin A and 308
(asialoglyco-octapeptides A^M and A^N) ^{13}C NMR data 321–323
T_N antigen (synthetic)
^{13}C NMR data 321, 322
structure 320
^{99}Tc quadrupole relaxation 379
Thymidylate synthetase ^{13}C(enriched)NMR 9
^{47,49}Ti quadrupole relaxation 381
p-Toluenesulphonyl fluoride, [methyl-^{13}C] modification of chymotrypsin 29
Transition metal nuclides NMR studies 340
^{59}Co 341
^{63}Cu 343
^{199}Hg 343
^{138,139}La 341, 366, 372, 374, 387
^{195}Pt 342, 383
^{99,101}Ru 342, 379
^{45}Sc 341, 366
^{89}Y 341
^{67}Zn 343, 366, 372, 374, 378
Trimethoprim binding to DHFR 21, 22, 24, 25
α-*N*-Trimethylalanine in myosin 154
Trypsin ^{13}C NMR *see also* Serine proteases
active site chemical modification 28
cryoenzymological conditions, acyl intermediates 46–48
cryosolvents for 44
inhibition by APPA 37–39
inhibition by Z-lys-CMK 34–38
reaction catalysed 27
Trypsin inhibitor
^{13}C enrichment 8
mode of action studies 34
Tyrosine
COSY ^{1}H spectrum 126
DQ ^{1}H spectrum 127
Tunable spectrometer compared with field cycling 211

^{235}U–^{19}F coupling 300

V
protonation 386
quadrupole relaxation 379

WALTZ-16 79, 80, 102, 103
Water
  behaviour in hydrous melts 351, 352
  exchange of hydrated cations 392
  ^1H exchange in 261, 262, 269
  orientation around F^- 352
  -water association 350, 351

Zero-field NMR 255–258